

## THERMODYNAMIC BEHAVIOUR OF MILD STEEL CORROSION IN AN ENVIRONMENT OF *BILBERRY CACTUS* PLANT EXTRACTS IN HYDROCHLORIC ACID SOLUTION

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### ABSTRACT

The inhibitive action of *bilberry cactus* plant extracts (BCPE) on mild steel in 1.5 M Hydrochloric acid with addition of different concentrations (0.1-0.5 g/l) was investigated using weight loss and hydrogen evolution measurement methods. The inhibitor organic structures were characterized for their functional groups using Gas Chromatography Mass Spectrometer (GCMS) and Fourier Transformation InfraRed (FTIR) analyses. The results revealed that the protective film formed on the surface of mild steel by the adsorption of extracts in 1.5 M HCl solution obeyed Langmuir adsorption isotherm. It was observed from thermodynamic adsorption parameters ( $\Delta H_{ads}$ ,  $\Delta S_{ads}$ , and  $\Delta G_{ads}$ ) that the inhibitor adsorbed via physical adsorption and the negative values obtained indicate exothermic reaction and spontaneous process. Finally, the effect of substituents type in inhibition efficiency was investigated using Linear Free Energy Relationship (Hammett relationship) and the reaction of adsorption favored by electron donation of the extract substituent groups.

**Keywords:** *Bilberry cactus, Mild steel, Inhibitor, Hammett relationship.*

### 1. INTRODUCTION

Mild steel is an iron alloy that contains less than 0.25% carbon. The steel is very reactive and will readily revert back to iron oxide (rust) in the presence of water, oxygen and ions [1]. The readiness of steel to oxidize on exterior exposure means that it must be adequately protected from the elements in order to meet and exceed its design life. Prior to painting and coating, new mild steel surfaces should be treated for mill scale, rust, sharp edges, laminations, burr marks and welding flux, forming or machine oils, salts, chemical contamination or mortar splashes on them, all of which must be removed to avoid sudden breakdown or failure of the steel during construction and fabrication process. Corrosion of steel is an electrochemical reaction that requires the presence of water (H<sub>2</sub>O), oxygen (O<sub>2</sub>) and ions such as chloride ions (Cl<sup>-</sup>), all of which exist in the atmosphere. This electrochemical reaction starts when atmospheric oxygen oxidizes iron in the presence of water. The mitigation of metallic corrosion by organic inhibitors is

a very active field of research [2]. It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen [3, 4]. Many researchers reported that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which related to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [5, 6]. Recently, environmental regulations on industrial consumption and development of new corrosion inhibitors have tightened up. Thus, natural products, non-toxic and environmental- friendly products, have gained much attention in regard to the development of green corrosion inhibitors that have high inhibition efficiency. Therefore, in this work, we attempted to find new environment friendly inhibitors [7]. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors. The toxic effect does not only

affect living organisms but also poisons the environment [8]. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors [9]. Inhibitors in this class are those which are environmentally friendly and are got from natural products [10].

Biberry cactus plant (BCP) is tree-like, much-branching plants with few prominent ribs. The bilberry plant is one of the most common plants in cultivation which quickly grow in temperate climates. The BCP species are widespread in Mexico including the Baja California peninsula and some Africa country. One of the species plant extract such as spinning cactus (*Opuntia fica indica*) was found to contain phytochemical compounds which was efficient to stop corrosion attack on mild steel with acid solution. It was reported that *Opuntia fica indica* extract, *Aleo eru* leaves orange and mango mango peels give adequate protection to steel in 5 % and 10 % HCl at 25 and 40 °C [11].

## 2.0 MATERIALS AND METHODS

### 2.1 Preparation of Metal Specimen

The mild steel sample obtained has chemical composition of carbon 0.053 %, Silicon 0.14%, Aluminium 0.2 %, Calcium 0.1 %, Manganese 0.48 %, Iron 97.48 %, Copper 0.057 % and Chromium 0.018 %. The mild steel specimens were mechanically cut in to dimension of 2.0 x 0.2 x 2.5 cm (with a surface area of 11.8 cm<sup>2</sup>). Prior to all measurement, the mild steel coupons were mechanically polished with series of emery paper from 400 to 1200 grades. The specimen were washed thoroughly with distilled water, degreased with absolute ethanol, dipped into acetone and dried in air. The dried specimens were stored in desiccators before use. The 1.5 M HCl solution was prepared by dilution of analytical grade 37 % HCl with double distilled water.

### 2.2 Preparation of Inhibitor (BCPE)

The fresh plant was abundantly collected at Bosso campus, Federal University of Technology, Minna, Niger State. The plant was shield dried and ground into powder.

105g of powdery samples were soaked in ethanol for 48hrs. The soaked samples were filtered and the extracts were obtained by rotary evaporator to expel the ethanol. The inhibitor (extract) obtained was prepared for phytochemical screening and dissolved in 1.5 M HCl to obtain the different concentrations (0.1 – 0.5 g/l) to carried out weight loss and hydrogen evolution measurements.

### 2.3 Phytochemical Analysis

The extracts obtained were analyzed at the National Research Institute of Chemicals Technology (NARICT), Zaria, Nigeria and results were printed from spectroscopy, to identify the compounds, functional groups and their structures. These tests were; Fourier Transformation Infrared (FTIR) analyses: CFLE was characterized by FTIR spectroscopy for identification of all active functional groups with FTIR-8400S instrument.

Gas Chromatography Mass Spectrometer (GCMS) analyses: CFLE also analyzed on GCMS-QP2010 PLUS SHIMADZU instrument, to detect all organic species present quantitatively.

### 2.4 Weight loss (WL) measurement

The weight of mild steel specimens was initially recorded and then they were immersed in the prepared aggressive solutions in the presence and absence of inhibitors concentrations. The specimens were retrieved at 2 h time interval, washed with distilled water, dipped acetone, and dry in air. The mild steel specimens were weighed again to determine the weight of the specimens after immersion and corrosion rate was determined with equation 1

$$\rho_{WL} = \frac{W_b - W_a}{A \cdot t} \quad (1)$$

Where:  $\rho_{wl}$  = Corrosion rate of weight loss ( $\rho_{WL}$ , gcm<sup>-2</sup>h<sup>-1</sup>),  $W_b$  and  $W_a$  are the Weight of mild steel specimen before and after immersion in the test solution respectively.  $A$  = surface area of the specimen and  $t$  is the end time of each experiment. The inhibition efficiency ( $IE_{wl}$  %) values was calculated

with equation 2 similar to equation used by [12].

$$IE_{wl}(\%) = \left( \frac{\rho_{wl}^{\circ} - \rho_{wl}}{\rho_{wl}} \right) \times 100 \quad (2)$$

Where:  $IE_{wl}(\%)$  is the Inhibition efficiency,  $\rho_{wl}^{\circ}$  and  $\rho_{wl}$  are Corrosion rate in absence and presence of concentrations of inhibitors respectively

### 2.5 Hydrogen Evolution (HE) measurement

Hydrogen evolution experiment was carried out in a gasometric setup, similar to the hydrogen evolution setup used by [12]. Mylius flask was replaced with conical flask (reaction vessel) containing prepared solution and mild steel specimens.

50ml of prepared corrodent solution was introduced in to the conical flask through a dropping funnel then removed. Degreased specimens of mild steel were carefully dropped into the solution and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of hydrogen gas was collected in calibrated tube by downward displacement of water over fixed time interval. A straight lines graph of  $H_2$  gas evolved per unit area against time were obtained. The slope of this line gave the rate of  $H_2$  gas evolved ( $\rho_{HE}, \text{mlcm}^{-2}\text{min}^{-1}$ ) and this is equivalent to corrosion rate of the mild steel specimens in absence and presence of different concentration of the studied inhibitors. Inhibition efficiencies were calculated using following equation which has been previously described [12].

$$IE_{HE}(\%) = \left( \frac{\rho_{HE}^{\circ} - \rho_{HE}}{\rho_{HE}^{\circ}} \right) \times 100 \quad (3)$$

Where:  $\rho_{HE}^{\circ}$  and  $\rho_{HE}$  are the Hydrogen evolution rates (corrosion rate) in absence and presence of concentrations of inhibitor.

The experiment was conducted at temperature range of 25-60°C



Figure 1: Hydrogen Evolution Setup

### 3 RESULTS AND DISCUSSION

The corrosion rate of mild steel in 1.5M hydrochloric with different concentrations of inhibitors from Table 1 showed that corrosion rate values were decreasing with increase in concentration of inhibitor as lower values obtained at 0.5g/l concentration are  $0.0013 \text{ gcm}^{-2}\text{h}^{-1}$  and  $0.0028 \text{ mlcm}^{-2}\text{min}^{-1}$  for weight loss and hydrogen evolution respectively. The high inhibition efficiency as corrosion rate reduce was as a result of occurrence of adsorption of inhibitor on mild steel. In hydrogen evolution measurement, it was observed that evolution rate decrease as concentrations of inhibitors increase and increase with rise in temperature. The values of inhibition efficiency decrease with rise in temperatures and increase as the concentrations of inhibitors increase. This behaviour results to desorption of inhibitors by undergoing decomposition due to temperature variation of the system, leading to weak efficiency of the inhibitor (extract) in the corrosive medium [13-15].

**Table 1: Different corrosion parameters obtained from both measurements at different temperatures**

Methods	Weight loss Measurement		Hydrogen evolution measurement		
	Corrosion parameters	Corrosion Rate	Inhibitor Efficiency	Hydrogen Evolution Rate	Inhibitor Efficiency
Tempe	Concentration				
25 °C	0	0.0124		0.0289	
	0.1 g/l	0.0036	70.83	0.0086	70.11
	0.2 g/l	0.0029	77.21	0.0065	77.65
	0.3 g/l	0.0021	82.9	0.0045	84.36
	0.4 g/l	0.0016	86.97	0.004	86.31
	0.5 g/l	0.0013	89.82	0.0028	90.22
30 °C	0	0.0133		0.0488	
	0.1 g/l	0.0043	66.92	0.016	67.05
	0.2 g/l	0.0037	71.64	0.0135	72.35
	0.3 g/l	0.0031	76.12	0.0116	76.32
	0.4 g/l	0.0024	81.6	0.0088	81.95
	0.5 g/l	0.0019	85.06	0.0075	84.6
40 °C	0	0.0143		0.0747	
	0.1 g/l	0.0051	63.98	0.0264	64.54
	0.2 g/l	0.0048	66.83	0.0246	67.02
	0.3 g/l	0.0035	75.24	0.0181	75.68
	0.4 g/l	0.0033	76.9	0.0162	78.27
	0.5 g/l	0.0026	81.16	0.0128	82.81
50 °C	0	0.0148		0.0901	
	0.1 g/l	0.0059	59.7	0.0358	60.31
	0.2 g/l	0.0053	64.06	0.0322	64.24
	0.3 g/l	0.0049	67.16	0.0291	67.65
	0.4 g/l	0.0046	69.12	0.0279	68.99
	0.5 g/l	0.0043	71.07	0.0262	70.87
60 °C	0	0.0155		0.1006	
	0.1 g/l	0.0086	44.76	0.0568	43.49
	0.2 g/l	0.0079	48.9	0.0524	47.83
	0.3 g/l	0.0076	51.2	0.0496	50.72
	0.4 g/l	0.0067	56.77	0.0442	56.02
	0.5 g/l	0.0063	59.5	0.0418	58.43

### 3.1 Thermodynamic Adsorption Parameters

Thermodynamic adsorption parameters show the interaction between the adsorbed molecule and electrode surface (mild steel). Adsorption strength can be deduced from the adsorption isotherm, which shows the equilibrium relationship between concentrations of inhibitors on the surface [16]. To evaluate the nature and strength of adsorption, the experimental data are fitted

to the isotherm, and from the best fit, the thermodynamic data for adsorption are evaluated. The data obtained from corrosion and hydrogen evolution rate were fitted in Langmuir adsorption isotherm and graph was plotted to obtain equilibrium constant of adsorption process using given expression:

$$C_{inh}\theta^{-1} = \frac{1}{K} + C_{inh} \quad (4)$$

Where  $\theta$  is surface coverage ( $\theta = \text{IE} \% / 100$ ),  $K$  is the equilibrium constant of adsorption process, and  $C_{inh}$  is concentration of the inhibitor.

Figure 2 represent the Langmuir isotherm for investigated inhibitor (extract) at different temperatures. The slope is taking to be unity and value of  $K$  was obtained from the intercept of the graphs.

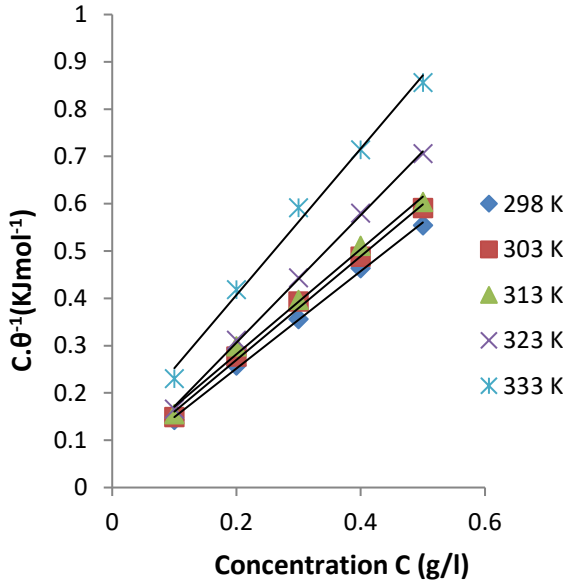


Figure 2: Langmuir Isotherm for BCPE extract at all Investigated temperatures

The equilibrium constant ( $K$ ) value was determine from the intercept of each Langmuir isotherm graphs and was related with free energy of adsorption ( $\Delta G_{ads}$ ) in equation 5 as given by [17, 18].

$$\Delta G_{ads} = -RT \ln(55.5K) \quad (5)$$

Where  $\Delta G_{ads}$  ( $\text{KJmol}^{-1}$ ) is free energy change of adsorption,  $R$  is universal gas constant ( $R=8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ),  $T$  is the Temperature of the system ( $\text{K}$ ) and  $K$  is the equilibrium constant ( $\text{l/g}$ ).

Gibbs free energy change had been related with other thermodynamic parameters in line with the basic thermodynamic equation to evaluate the values of enthalpy change

( $\Delta H_{ads}$ ) of adsorption with application of Van't Hoff equation and hence the enthalpy change ( $\Delta H_{ads}$ ) of adsorption are estimated graphically from  $\ln K_{ads}$  vs  $1/T$  plot (Figure 3) and the corresponding entropies of adsorption ( $\Delta S_{ads}$ ) were calculated with equation 6 [19]:

$$\ln K_a = -\frac{\Delta H_{ads}}{2.303RT} + \text{Constant} \quad (6)$$

The straight line graph of  $\ln K$  against  $1/T$  was plotted for each corrosion measurement and the change in enthalpy ( $\Delta H_{ads}$ ) was determined with Slope  $= -\frac{\Delta H_{ads}}{2.302R}$ .

From the thermodynamic point of view, the famous equation 10 that relate change in free energy of adsorption ( $\Delta G_{ads}$ ), change in enthalpy ( $\Delta H_{ads}$ ) and temperature of adsorption was used to evaluate entropy change ( $\Delta S_{ads}$ ) of adsorption:

$$\Delta S_{ads} = (\Delta H_{ads} - \Delta G_{ads}) / T \quad (7)$$

The values obtained for Thermodynamic adsorption parameters for both weight loss and hydrogen evolution measurement are listed in the Table 2

High values of equilibrium constant ( $K$ ) are 21.64  $\text{l/g}$  and 21.74  $\text{l/g}$  at 25  $^{\circ}\text{C}$  obtained for weight loss and hydrogen evolution respectively, similar to values obtained by [19] indicating strong adsorption character of BCPE on the surface of mild steel.

The Gibbs free energy ( $\Delta G_{ads}$ ) values obtained are negative as shown in Table 2 and this indicate the adsorption of inhibitor on mild steel surface is spontaneous process. Similar values was reported by [20] that values of Gibbs free energy ( $\Delta G_{ads}$ ) less than and equal to  $-20 \text{ KJmol}^{-1}$  are consistent with electrostatic interaction between the electrolyte (charged molecules) and the electrode (charged metal surface) which categorize as physisorption adsorption behavior.

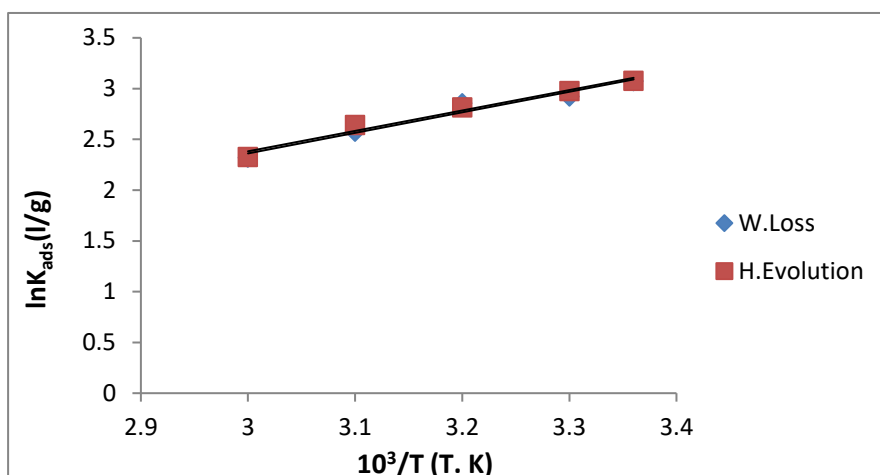


Figure 3: Graph of  $\ln K$  against  $1/T$  for Mild steel in test solution of studied inhibitor with 1.5M HCl

But when the value is greater and equal to  $-40\text{KJmol}^{-1}$ , it involve charge sharing or transfer of charges from charged molecule (inhibitor) to the metal surface and this form coordinate type of bond called chemisorptions adsorption behavior. It is observed from the values obtained for Gibbs free energy ( $\Delta G_{ads}$ ), that it is less than  $-20\text{KJmol}^{-1}$  which indicate the studied inhibitor obeyed physical adsorption mechanism.

The obtained values for change in enthalpy ( $\Delta H_{ads}$ ) are also negative for studied inhibitor and this implies that the adsorption of inhibitor molecule on the surface of mild steel is an exothermic reaction. [21] reported that for an exothermic reaction, a lower value is obtained and this distinguishes it from chemisorptions adsorption.

It has been established that bond enthalpies are independent of the compound in which they appear and quantitatively denote physisorption if  $\Delta H_{ads} < 0$  (i.e exothermic reaction, usually associated with formation of new bonds and evolution of heat). On the other hand, chemisorptions (bond breaking energies, usually involving absorption of heat) may be inferred if  $\Delta H_{ads} > 0$  [19].

The values of change in enthalpy ( $\Delta H_{ads}$ ) obtained are less than zero, and it implies the formation of a covalent type of bond in the physisorbed layer. Change in entropy ( $\Delta S_{ads}$ ) value generated was negative which shows is less than zero. As observed from the Table 3, the value decreases with increase in temperature and this is as a result of the inhibitors added in the system which set in orderliness in reaction of the acid solution with mild steel.

Table 2: Thermodynamics adsorption parameters of BCPE inhibitors HCl

Measurement	Temperature	K (l/g)	$\Delta G_{ads}$	$\Delta H_{ads}$	$\Delta S_{ads}$
Weight loss	25 °C	21.64	-17.48	-38.7	-0.064
	30 °C	18.59	-17.41	-38.7	-0.064
	40 °C	17.38	-17.88	-38.7	-0.06
	50 °C	13.16	-17.71	-38.7	-0.059
	60 °C	10.19	-17.55	-38.7	-0.058
Hydrogen Evol.	25 °C	21.74	-17.58	-38.51	-0.07
	30 °C	19.64	-17.62	-38.51	-0.069
	40 °C	16.72	-17.78	-38.51	-0.066
	50 °C	14.03	-17.88	-38.51	-0.064
	60 °C	10.25	-17.56	-38.51	-0.062

It was reported that the active ingredients of the extracts are assumed to be more in disorder (chaotic) prior to adsorption with inhibitors [22]. But as the adsorption on the metal surface commences with addition of inhibitors, orderliness gradually sets in and this leads to lower entropy values as it is obtained for the studied extracts.

### 3.2 Corrosion Kinetic Parameters.

Arrhenius equation is used to evaluate the temperature dependence of apparent activation energy and frequency factor (A) as follow:

$$\log \rho = \log A - \frac{E_{app}}{2.303 \times RT} \quad (8)$$

Where  $E_{app}$  is the apparent activation energy with unit in KJ/mol,  $\rho$  is the corrosion rate of mild steel, A is the frequency factor which has the same unit with corrosion rate ( $\text{gcm}^{-2}\text{min}^{-1}$  &  $\text{mlcm}^{-2}\text{min}^{-1}$ ), R is the gas constant ( $R= 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and T is the absolute temperature (K). Graph of  $\log \rho$  against  $1/T$  gave straight line, where slope and intercept was obtained. The slope of the lines is considered to be equal to  $-\frac{E_{app}}{2.303 \times R}$  and the intercept of the line was extrapolated at  $1/T = 0$ , equal to  $\log A$  [12, 14, 21, 22].

However, the values of change in enthalpy and change in entropy for the formation of activation complex were obtained with transition state equation as given [12, 14]:

$$\log \left( \frac{\rho}{T} \right) = \left[ \left( \log \left( \frac{R}{hN} \right) \right) + \left( \frac{\Delta S}{2.303R} \right) \right] - \frac{\Delta H}{2.303RT} \quad (9)$$

Where N is Avogadro number ( $N= 6.022 \times 10^{23}$ ), h is Planck constant ( $h= 6.626 \times 10^{-34}$ ), R is gas constant ( $R= 8.314 \text{ Jmol}^{-1}$ ), T is the temperatures in the system,  $\rho$  is the corrosion rate ( $\text{gcm}^{-2}\text{h}^{-1}$  or  $\text{mlcm}^{-2}\text{min}^{-1}$  depend on methods used),  $\Delta S$  is change in entropy ( $\text{KJmol}^{-1}$ ) and  $\Delta H$  is change in enthalpy ( $\text{KJmol}^{-1}$ ).

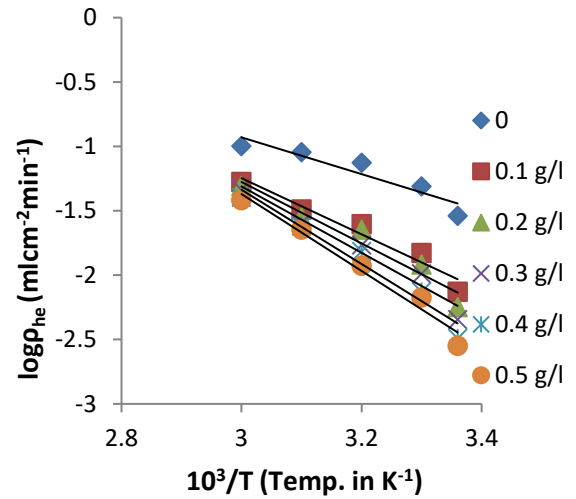
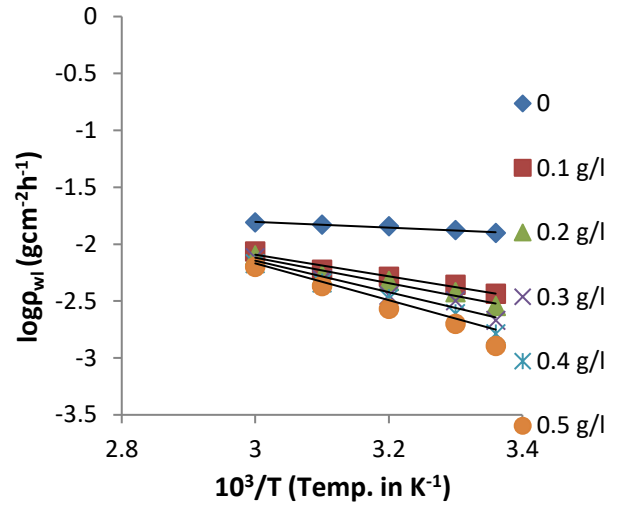


Figure 4: Arrhenius graphs of mild steel corrosion rate for both adopted measurement

Graph of  $\log \left( \frac{\rho}{T} \right)$  against  $1/T$  is plotted to obtain slope and intercept values. The slope is equal to  $-\frac{\Delta H}{2.303RT}$  from the transition state equation and intercept is equal to  $\left[ \left( \log \left( \frac{R}{hN} \right) \right) + \left( \frac{\Delta S}{2.303R} \right) \right]$  from which values of  $\Delta H$  and  $\Delta S$  are calculated respectively. Figure 5 represent the transition state graph of mild steel corrosion in the absence and presence of bilberry cactus plant extract (BCPE) for both log values of corrosion and hydrogen evolution rates.

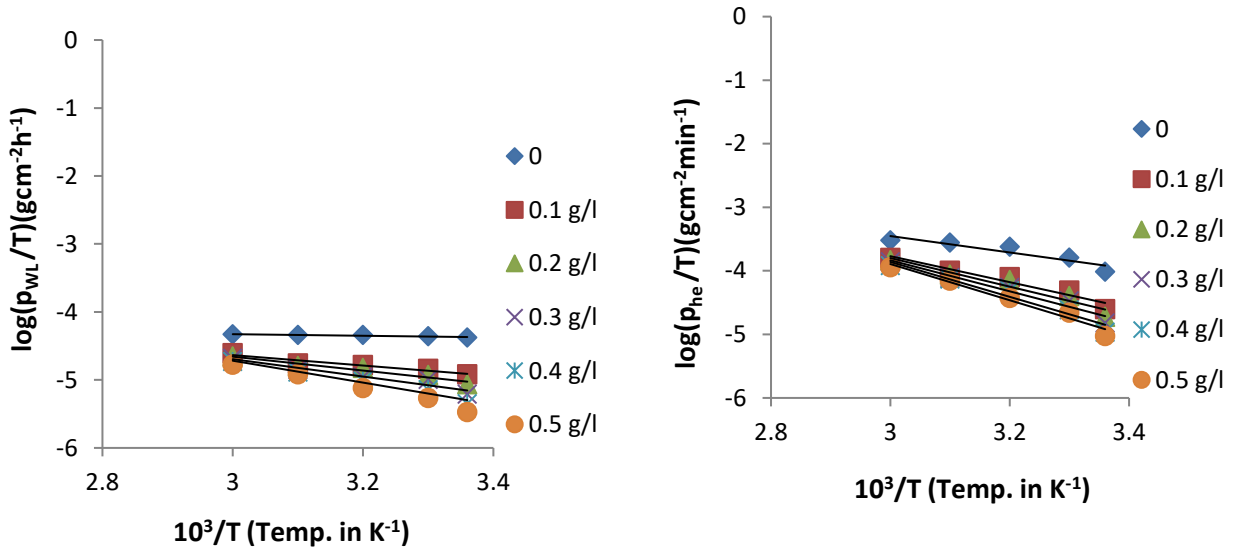


Figure 5: Transition state graphs of mild steel corrosion rate for values obtained from both measurements

**Table 3: Corrosion Kinetic Parameters for mild steel in 1.5 M HCl in the absence and presence of BCPE**

Weight Loss	Conc.	A (gcm <sup>-2</sup> h <sup>-1</sup> )	E (Kjmol <sup>-1</sup> )	ΔH (Kjmol <sup>-1</sup> )	ΔS (Jmol <sup>-1</sup> K <sup>-1</sup> )
	0	0.089	4.83	2.24	-273.71
	0.1 g/l	5.717	18.19	15.6	-239.14
	0.2 g/l	17.314	21.42	18.84	-229.93
	0.3 g/l	101.861	26.51	23.91	-215.19
	0.4 g/l	479.09	30.95	28.36	-202.32
	0.5 g/l	2376.67	35.53	32.94	-189.00

Hydrogen Evol.	A (gcm <sup>-2</sup> min <sup>-1</sup> )	E (Kjmol <sup>-1</sup> )	ΔH (Kjmol <sup>-1</sup> )	ΔS (Jmol <sup>-1</sup> K <sup>-1</sup> )
0	2.22X10 <sup>3</sup>	27.30	24.71	-189.56
0.1 g/l	1.39X10 <sup>5</sup>	40.61	38.02	-155.14
0.2 g/l	6.13X10 <sup>5</sup>	44.84	42.25	-142.83
0.3 g/l	4.58X10 <sup>6</sup>	50.59	48.00	-126.10
0.4 g/l	1.10X10 <sup>7</sup>	53.22	50.63	-118.84
0.5 g/l	8.42X10 <sup>7</sup>	58.97	56.38	-101.90

It can be observed from Table 3 that as the concentration of inhibitors increases, the apparent activation energy increases and this indicates high inhibition efficiency of the activation energy similar to apparent activation energy reported by [23]. Further observation revealed  $E_a$  (inhibited) >  $E_a$  (uninhibited) coupled with decrease in inhibition efficiency with increase in temperature have been ascribed to physical adsorption mechanism [24, 25]. Similar trend of apparent activation energy value was obtained for frequency factors in which,

the value increases with increase in concentration of inhibitors [15].

It is also noticed that the apparent activation energy ( $E_{app}$ ) is greater than change in enthalpy ( $\Delta H$ ) value and this is approximately equal to product of Gas constant (R) and temperatures of the system. This is in line with thermodynamic unimolecular reaction as reported by [26]. As given in the expression below;

$$\bullet \quad E_{app} - \Delta H = RT \quad (10)$$

Therefore, the studied mild steel corrosion in 1.5M HCl in presence and absence of



different concentration of inhibitors follows the character of unimolecular reaction.

The negative values obtained for change in entropy ( $\Delta S$ ), implies that disorderliness occur in inhibited and uninhibited system and form association with mild steel. The same behaviour of change in entropy ( $\Delta S$ ) was reported by [12] that the activation complex in the determining step represent association rather than dissociation step, meaning a decrease in disorder take place on going from reactant to activated complex [27].

#### 4 ADSORPTION MECHANISM

The inhibition efficiency has been found to be closely related to inhibitor adsorption abilities and molecular properties for different kinds of organic compounds [28–30]. The inhibiting mechanism was generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface [31]. Organic plant comprises of some phytochemical compound which contributed to the inhibition of corrosion on mild steel when attacked by a corrosive media. [4]

The inhibition effects of plant extracts are due to the presence of tannin, steroids, saponins, alkaloid, glycosides and amino acids [32-33].

From the phytochemical screening result obtained it was revealed that BCPE contained Flavanoids, alkaloids, tannins and large amount of Saponins compounds with high percentage hydroxyl (OH) groups as reported by [34]. The functional groups present in the compounds was further explained with Fourier Transformation Infra Red (FTIR) and Gas Chromatography Mass Spectroscopy (GCMS) as given in Figure 4 and 5.

Figure 7 depicts the chromatogram of bilberry cactus plant extract (BCPE) where all organic species were detected quantitatively equivalent to the peak. It was reported that the peaks were proportional to the amount of the organic compounds formed [35]. Structural assignment of GC retention data of compounds is based on spectral matching with NIST library (National Institute of Standards and Technology).

The result of BCPE chromatogram revealed the presence of nine phytochemical compounds in which name of the compounds was selected base their molecular weight that depends on structures of the molecules. It has been established that the inhibition property of these compounds is attributed to their molecular structure [4]. The nine phytochemical compounds are listed with their structures shown in Table 4;

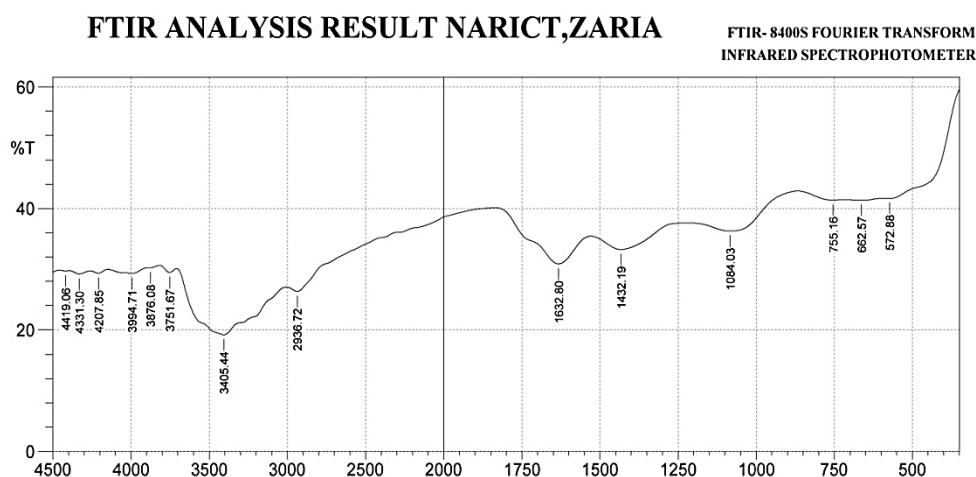


Figure 6: Fourier Transformation Infrared (FTIR) for BCPE

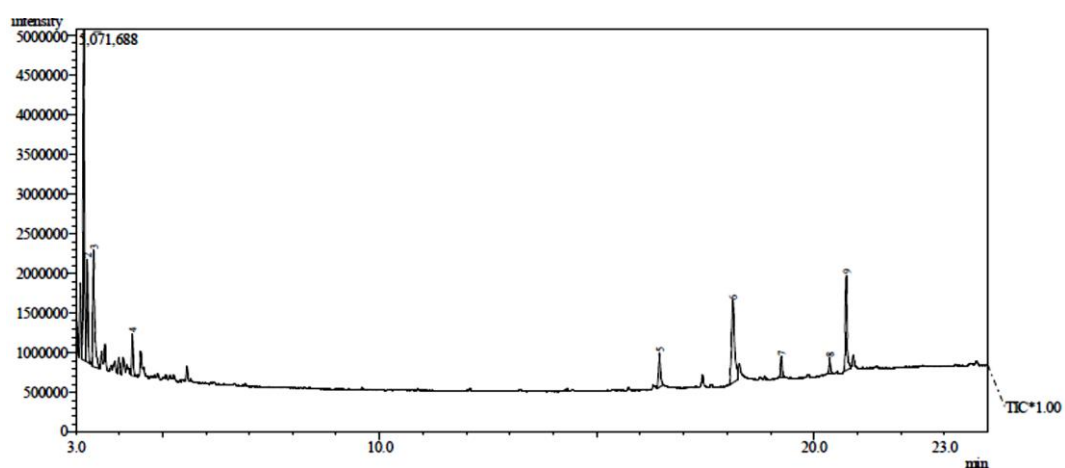


Figure 7: GCMS of BCPE

Table 4: Names of Phytochemical Compounds and their structures obtained from GCMS

Compounds Name	Structure
Ethylbenzen	
2-Methylundecane	
1, 4-dimethylbenzen	
2-Methylhepadcane	
Nonadecanoic acid	
13-Docosenoic acid	
Ttradecyl 2,2,3,3,3-Pentafluoropropanoate	
3,11-Teradecadien-1-ol	
9,12-Octadecadienoyl chloride	

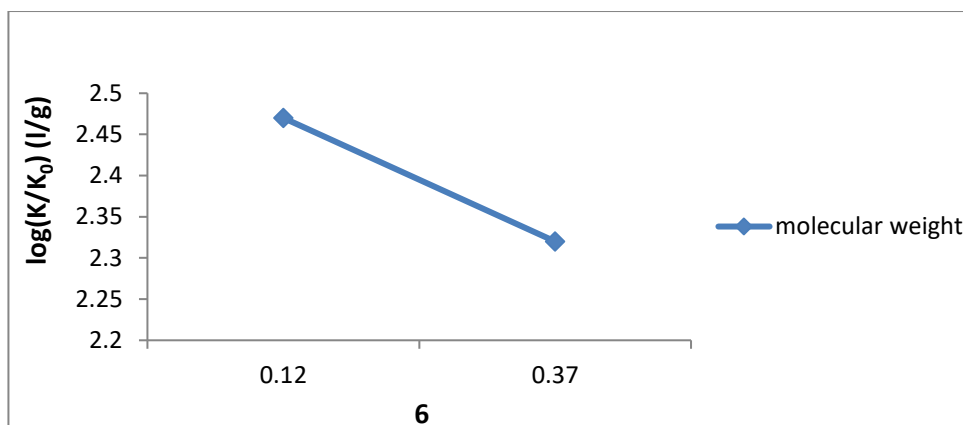


Figure 8: The Linear free energy relationship (LFER) between  $\log\left(\frac{K}{K_0}\right)$  and Hammett constant for studied inhibitors on mild steel in contact with 1.5M HCl

Most of corrosion inhibitors are organic compound having hetero atoms in their aromatic or long carbon chain. It has been known that the organic molecules can adsorbed at the metal- solution interface, which inhibits the corrosion on the metal surface [36]. The strength of adsorption depends on the charge on this anchoring group [rather on the hetero atom (i.e., atoms other than carbon including nitrogen, sulphur) present in the anchoring group]. Most organic inhibitors possess at least one functional group, regarded as the reaction center or anchoring group [16]. The anchoring groups (functional groups) were characterized with the FTIR spectroscopy in Figure 7. The FT-IR spectrum was observed with some broad peaks, indicating the presence of the functional groups [35]. It has been established that the bands frequency changed in adsorption process and probably leads to missing of some functional groups [35]. In any case, adsorption molecules spread over the metal surface and the resulting adsorption layer function as a barrier, isolating the metal from the corrosion [37].

#### 4.1 Effect of Substituent Groups

Substituents are the chemical compounds in the inhibitors (extracts) that contributed to electron donating or withdrawing ability in inhibition process [16]. The substituent type can only be analyzed or described by Hammett substituent parameters. As it is reported, that substituent type is evaluated

with linear free energy relationship (LFER) or Hammett equation, as given [38-43].

$$\log\left(\frac{K}{K_0}\right) = \rho\sigma \quad (11)$$

It has been established that  $K/K_0$  are considered to be the average value of the equilibrium constant of adsorption for studied inhibitor [12]. In the present work,  $K/K_0$  was considered as largest molecular weights of functional groups among the structures obtained for the studied extract.  $\rho$  is the reaction constant that measure how sensitive a particular reaction is to change the electronic effect of substituent groups.  $\sigma$  is substituent constant which refers to the observed electronic effect that a particular substituent impact to a molecule. From the GCMS result the highest molecular weight obtained are 298 and 210 for 3,11-Teradecadien-1-ol and 9,12-Octadecadienol chloride respectively. It can be observed from the two compounds structures that the functional groups are Hydroxyl (OH) and Chloride (Cl) groups. The substituent constant generated for OH and Cl groups are 0.12 and 0.37 as reported by (Jaffe, 1953; Mullins *et al.*, 2004; Maskill, H., 1985) and the values were used to evaluate reaction constant values through the slope obtained from graph of linear free energy relationship (LFER) between  $\log\left(\frac{K}{K_0}\right)$  and the Hammett constant for the studied inhibitors on mild steel in 1.5M HCl. The log values of both molecular weights are 2.47 and 2.32 for hydroxyl and chloride respectively.

The slope obtained from Figure 8 is -6 and is equivalent to reaction constant. It has been stated that, the reaction constant ( $\rho$ ) depends on the nature of the chemical reaction as well as the reaction conditions (solvent, temperature). Both the sign and magnitude of the reaction constant are indicative of the extent of charge build up during the reaction progress. Reactions with  $\rho > 0$  are favoured by electron withdrawing groups (i.e., the stabilization of negative charge). Those with  $\rho < 0$  are favoured by electron donating groups (i.e., the stabilization of positive charge). The greater the magnitude of reaction constant ( $\rho$ ), the more sensitive the reaction by electronic substituent effects [38, 41].

However, the values of reaction constant for the investigated inhibitors showed less than zero and this indicated the reaction was favored by electron donating groups which imply the stabilization of positive charges.

## CONCLUSION

The Inhibition efficiency of the studied green inhibitor increased with increase in concentration but decreased with increase in temperature. The experimental data obtained showed there was a good agreement between the results obtained in both measurements. The value of apparent activation energy in inhibited system is more than the value in uninhibited system. The inhibition process obeyed the Langmuir adsorption model at all investigated temperatures. Thermodynamic adsorption parameters ( $\Delta H_{ads}$ ,  $\Delta S_{ads}$ , and  $\Delta G_{ads}$ ) showed that the adsorption was a spontaneous process, and that occurrence of exothermic reaction and the low values of entropy result in formation of ordered stable complex film on the metal surface. Finally, Hammett relationship showed the performance of the studied organic plant extracts and it inhibited corrosion by electron donation properties of the substituent groups.

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